

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 February 2003 (13.02.2003)

PCT

(10) International Publication Number
WO 03/011440 A1

(51) International Patent Classification⁷: B01D 63/00,
61/36, C12G 3/08, C12H 1/16

(21) International Application Number: PCT/IT02/00472

(22) International Filing Date: 18 July 2002 (18.07.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
VI2001A000161 31 July 2001 (31.07.2001) IT

(71) Applicant (for all designated States except US): ENO-
LOGICA VASON S.R.L. [IT/IT]; Località Nassar 37,
I-37020 Pedemonte (IT).

(72) Inventor; and

(75) Inventor/Applicant (for US only): FERRARINI,
Roberto [IT/IT]; Via Cavarena, 6, I-37020 Fumane (IT).

(74) Agents: GALLO, Luca et al.; Jacobacci & Partners S.p.A.,
Via Berchet, 9, I-35131 Padova (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

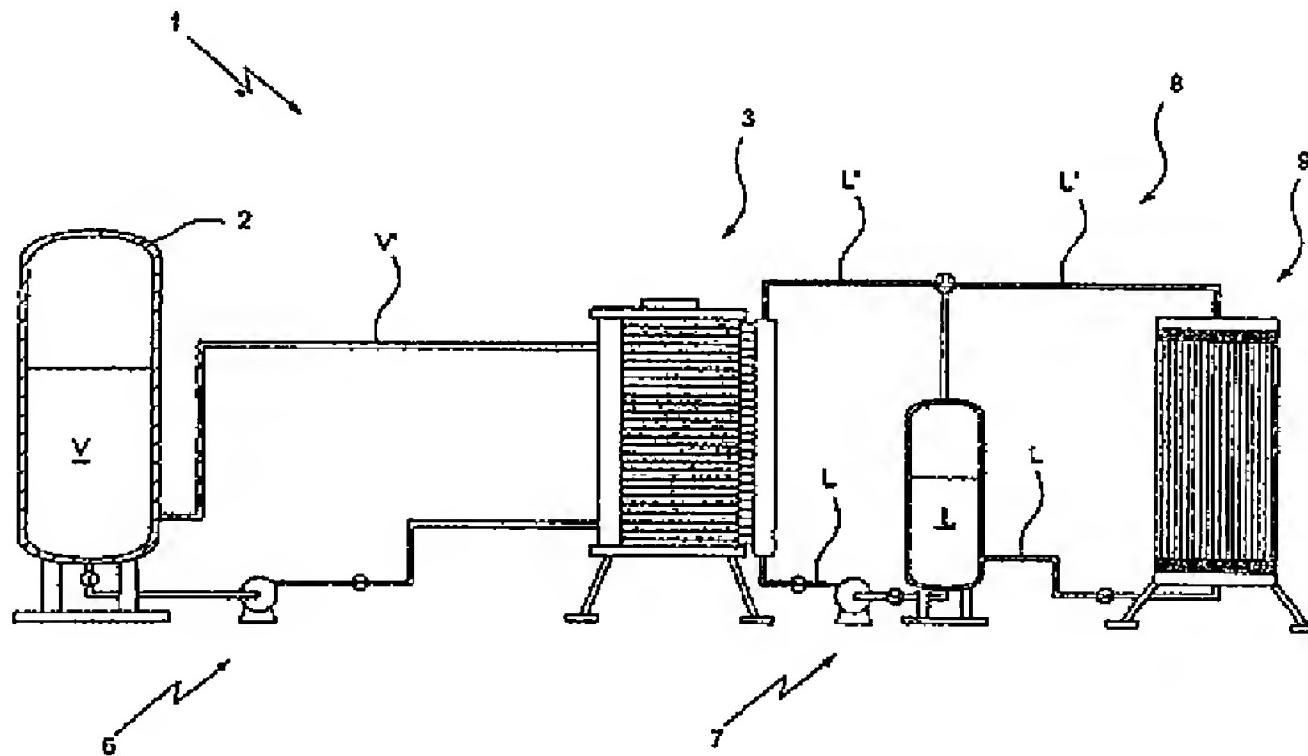
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS AND PLANT FOR THE SEPARATION OF UNDESIRABLE SUBSTANCES FROM ALIMENTARY LIQUIDS, IN PARTICULAR FROM WINE



WO 03/011440 A1

(57) Abstract: Plant for the separation of undesirable substances from alimentary liquids, in particular from wine, which comprises a unit (3) with hydrophobic membranes having holes for trapping gas, supplied with wine to be treated (V) by means of first circulation means (6) and with an extraction fluid (L) having an alcoholic content substantially similar to that of the wine to be treated (V), by means of second circulation means (7). The two fluids pass along the two sides of the membranes, allowing the removal of the undesirable volatile substances which pass through the latter. The extraction fluid (L) is made to circulate by the second means (7) inside a purification circuit (8) which comprises a unit (9) for separation of the volatile substances, consisting preferably of an ion-exchange column. The process implemented in particular by the above mentioned plant envisages a step involving preparing the wine to be treated (V) inside a container (2), a subsequent step involving conveying to the above mentioned unit (3) and then a step involving removal of the undesirable volatile substances contained therein by means of evaporation, diffusion and consequent evaporation thereof which causes them to pass through the membranes so as to be then evacuated by the extraction fluid (L) by means of ion-exchange resins, distillation, adsorption onto polymers or other system.

PROCESS AND PLANT FOR THE SEPARATION OF UNDESIRABLE SUBSTANCES FROM ALIMENTARY LIQUIDS, IN PARTICULAR FROM WINE
DESCRIPTION

Technical field

The present invention concerns a process and a plant for the separation of undesirable substances from alimentary liquids, in particular from wine. The invention in question is intended to be advantageously used in the oenology sector for the refinement of wine, namely in order to improve the organoleptic properties and taste thereof or reduce certain components which are present in excessive amounts.

Background art

At present, as is known, the wine industry makes widespread use of microfiltration plants, or submicronic filtration (ultrafiltration or nanofiltration) plants, which use semipermeable membranes generally formed by thin polymer films in order to separate some components from others.

The passage of the wine to be filtered through the membrane is usually obtained by means of mechanical overpressure. These membrane-type filtration plants have major operational limitations in that they do not allow the separation of all the undesirable components, for example because of their dimensions which in some cases are excessively small, their polarity or their surface tension. These plants, therefore, are suitable only for implementing

given filtration processes of the type for example described in the patents IT 1,249,187 and IT 1,242,866.

Moreover, numerous plants based on the principle of (direct or reverse osmosis) are known, said plants being able to achieve, by means of a semipermeable membrane, purification of solutions, separating a permeated fraction from a retained fraction. Reverse osmosis in particular is a known dual-action process which allows, on the one hand, the purification of solutions, eliminating undesirable substances (for example salts) and, on the other hand, the concentration of solutions, extracting water or other solvent from the initial product.

In the oenology sector, reverse osmosis is currently used in methods for concentrating wine or fruit juices with a low sugar content, as described in the patent US 3,979,521, or in order to extract volatile esters with a low molecular weight (such as, for example, methyl-anthranilate) from wine or must, as described in the patent US 4,401,678, or in order to remove water or a more or less important part of alcohol from wine as described in the patents US 4,999,209, US 4,888,189, US 4,681,767, FR 2,653,443, GB 2,133,418, IT 1,242,865, WO/03902 and WO/08783.

A method and an apparatus for the treatment of fluids and in particular wine, able to separate a retained

fraction from a permeated fraction in a reverse osmosis unit, is also known from the American patent No. US 5,480,665. The latter receives inside it the undesirable substances such as, for example, the volatile acidity components (ethyl acetate and acetic acid) which are then removed by means of a subsequent treatment. For this purpose, the permeated fraction is passed through an adsorbent column able to remove the acetic acid by means of anion-exchange resins and the ethyl acetate by means of hydrolysis.

With this treatment it is therefore possible to purify, of the undesirable substances, the permeated fraction which is then reintroduced into the wine, obtaining a final product which is substantially devoid of volatile acidity. Advantageously, this method envisages also treating the permeated fraction with a low-temperature distillation process in order to remove CO₂, H₂S, acetaldehyde or other volatile components.

Methods for treating wine in order to lower the total acidity by means of ion-exchange resin columns are per se already known and for example described and illustrated in the patent US 4,205,092.

The processes for separation of undesirable substances briefly described hitherto have in practice proved to be unsatisfactory in terms of performance. In other words,

with these processes and associated plants it is not possible to select adequately only the undesirable substances, and therefore inevitably also substances - which instead make a positive contribution to the quality 5 of the wine - are removed together therewith.

Disclosure of the invention

In this situation the task underlying the present invention is to eliminate the drawbacks of the abovementioned prior art by providing a process and a plant 10 for the separation of undesirable substances from alimentary liquids, in particular from wine, which allow an improvement in the quality of the product obtained by means of an improved action involving selective purification of only the undesirable substances.

Another object of the present invention is that of 15 providing a process and a plant for the separation of undesirable substances from alimentary liquids, in particular from wine, which is constructionally simple and operationally entirely reliable.

These and other objects are all achieved by a process 20 for the separation of undesirable substances from alimentary liquids, in particular from wine, which is characterized in that it comprises the operating steps of: preparing a wine to be treated inside a container; 25 conveying the wine to be treated to a filtration unit

provided with hydrophobic membranes having holes for trapping gas and able to be passed along, on a first side, by the wine to be treated and, on a second side, by an extraction fluid having an alcoholic content substantially similar to that of the wine to be treated and made to circulate in a purification circuit; removal of undesirable volatile substances from the wine to be treated by means of evaporation and subsequent diffusion thereof in the gas trapped in the membranes and consequent condensation of the volatile substances on the second side of the membranes, with the formation of a contaminated fluid formed by the extraction fluid and the permeated volatile substances and a retained fraction formed by the treated wine purified of the permeated volatile substances.

According to the invention the said objects are also achieved by means of a plant for the separation of undesirable substances from alimentary liquids, in particular from wine, characterized in that it comprises a container for the wine to be treated, a filtration unit provided with hydrophobic membranes having holes for trapping gas, first circulation means for conveying the wine to be treated through the filtration unit, causing it pass along a first side of the membranes; second circulation means for causing the flow of an extraction fluid having an alcoholic content substantially similar to

that of the wine to be treated in a purification circuit through the filtration unit, causing it to pass along the second side of the membranes; the membranes removing from the wine to be treated the undesirable volatile substances
5 by means of evaporation and subsequent diffusion thereof in the gas trapped in the membranes and consequent condensation thereof on the second side of the membranes, with the formation of a contaminated fluid formed by the extraction fluid enriched with the permeated volatile
10 substances, and a retained fraction formed by the treated wine purified of the volatile substances; the purification circuit supplying by means of the second circulation means at least one unit for separation of the volatile substances from the contaminated fluid.

15 This process and this plant allow an effective improvement in the quality of the wine treated and are particularly suitable for use with wines having an excessive volatile acidity content.

Brief description of the drawings

20 The technical characteristics of the invention, in accordance with the abovementioned objects, may be clearly determined from the contents of the claims below and the advantages thereof will emerge more clearly from the detailed description which follows, with reference to the
25 accompanying drawings, which show a purely exemplary non-

limiting example of embodiment thereof and in which:

FIG. 1 shows a functional logic diagram of the process and the plant for the separation of undesirable substances from alimentary liquids, in particular from wine, according
5 to the present invention;

FIG. 2 is a schematic illustration of the operating principle of the hydrophobic membranes used in the process and in the plant in question.

Detailed description of a preferred example of embodiment

10 With reference to the accompanying figures, 1 denotes in its entirety the plant for implementing a process for the separation of undesirable substances from alimentary liquids, in particular from wine, according to the present invention.

15 This plant 1 is intended to be used in the food industry in general, and in particular in the oenology sector, in order to treat a very large number of different types of alimentary liquids. Below, for the sake of simplicity of the description, reference will be made only
20 to the example of an oenological product such as wine or wine must, without, as a result, the use of this plant with other alimentary liquids departing from the protective scope of the present patent.

The plant 1 essentially comprises a container 2 for
25 wine to be treated V, a unit 3 which has hydrophobic

membranes 4 with holes 5 for trapping a gas G and the function and structure of which will be described more clearly below, and first circulation means 6 for causing the wine V to flow through the unit 3, causing it to pass along a first side 4' of the membranes 4.

The second side 4" of the membranes 4 is instead passed along by an extraction fluid L which is conveyed by second circulation means 7 inside a closed purification circuit 8. The extraction fluid L consists of a liquid solution having an alcoholic content substantially similar to that of the wine V which can be obtained, for example, as will be seen below, also with a part of wine devoid of undesirable substances.

The membranes 4, which are of the type marketed for example by GORE TEX or PALL and already known in the industrial sector and in the medical field, are hydrophobic, i.e. consist of hydrophobic polymers with a high molecular weight, generally polypropylene or polytetrafluoroethylene, forming a three-dimensional structure with pores having a diameter preferably in the region of a tenth of a micrometre able to retain inside them gas, generally consisting of air. This structure, as is known, is impermeable to water, but permeable to gases. These same membranes made of hydrophobic material (permeation membranes) differ from each generally in terms

of thickness, permeability to air, diameter of the pores, etc.

Fig. 2 shows in schematic form a membrane 4 of the type mentioned above, which is passed along tangentially, 5 on both sides 4', 4'', by the wine V and the extraction fluid L, respectively.

The passage, from one side to the other of the membrane 4, of one or more substances occurs substantially in accordance with the principle of (direct) osmosis 10 whereby a semipermeable membrane placed so as to make contact with and separate two solutions having a solute with different concentration allows, in given conditions, the through-flow of solvent from one side to the other of the membrane so as to re-establish an equal concentration 15 in the two solutions.

In the plant 1 and in the process in question, however, the membranes 4 of the type described above do not participate directly in the removal of the undesirable substances by means of a selective action due to their 20 intrinsic characteristics, as instead occurs in the case where osmotic membranes are used.

The membranes 4 used in the process and in the plant according to the present invention regulate the through-flow of the undesirable volatile substances which are 25 present in the wine in a greater concentration than in the

extraction fluid L by means a complex mechanism illustrated schematically in Fig. 2. This mechanism, which is known per se, envisages the evaporation of one or more undesirable volatile substances (for example acetic acid, ethyl acetate, acetaldehyde, volatile substances with an undesirable odour, etc.) on the first side 4' of the membrane 4, the diffusion therefore inside the gas G retained in the pores 5 and then the condensation thereof on the second side 4" of the membrane 4 so as to then be evacuated by the extraction fluid circulating in the purification circuit 8.

In accordance with the physical principle forming the basis of operation of the membrane, the through-flow of the volatile substances is regulated by the value of the partial pressures of the individual components in the two liquids on the sides of the membrane.

The action of the membrane 4 basically results in the formation of a contaminated fluid L', which is composed of the extraction fluid L enriched with the volatile substances which have passed through the membrane 4, and a retained fraction composed of the treated wine V' purified of the volatile substances.

At this point, in accordance with the diagram of the plant illustrated in Fig. 1, the contaminated fluid L' which advances in the purification circuit 8 is made to

pass through a separation unit 9 having the purpose of eliminating the volatile substances and regenerating in this way the extraction fluid L.

Advantageously the separation unit 9 may be formed by means of an anion-exchange resin filtration column (as indicated in Fig. 1) particularly suitable for removing acetic acid and/or ethyl acetate by means of basic sites having an electrostatic action with for example NH₃⁺ groups. Alternatively or in parallel the contaminated fluid L' may also be sent to a distillation column (not shown since it is of a type known per se) in order to extract acetaldehyde, or H₂S, or certain volatile esters responsible for unpleasant aromas. Obviously, the purification of the contaminated fluid may also be obtained by means of filtration processes involving ion-exchange resins or using other methods such as adsorption onto polymers, extraction with solvents, or the like.

The present invention also relates to a process for the separation of undesirable substances from alimentary liquids - in particular able to be implemented by means of the plant 1 described above - which is illustrated in the accompanying Fig. 1.

Operationally speaking, it comprises according to the invention the steps of preparing the wine V to be treated inside the container 2, subsequent conveying of a flow of

this wine V into the unit 3 described above and consequent removal therefrom of the undesirable volatile substances by means of the passage of the said substances through the hydrophobic membranes 4 in the manner described above.

5 These steps thus result in the formation of a contaminated fluid L' composed of the extraction fluid L and the undesirable volatile substances and a retained fraction formed by the treated wine V' purified of the said undesirable volatile substances.

10 At this point, the final step of re-introduction of the treated wine V' into the container 2 follows. This cycle is repeated until, inside the container, there is a concentration of the individual undesirable substances which is sufficiently low, for example less than a 15 predetermined threshold value.

Advantageously, in accordance with a further characteristic feature of the present process, the contaminated fluid L' is again subjected to a step involving conveying into the separation unit 9 indicated above, where it undergoes a step involving removal of the undesirable volatile substances. This is then followed by a step involving re-introduction of the regenerated extraction fluid L inside the purification circuit 8.

The step involving removal of the volatile substances from the extraction fluid L may be obtained by means of an 25

ion-exchange process or by means of a distillation process.

The invention thus conceived therefore achieves the predefined objects.

Obviously, during its practical realisation, the
5 invention may also assume forms and configurations
different from that illustrated above without thereby
departing from the present scope of protection.

Moreover, all the details may be replaced by
technically equivalent elements and the dimensions, forms
10 and materials used may be any according to requirements and
in particular both plastic and metal may be used.

CLAIMS

1. Process for the separation of undesirable substances from alimentary liquids, in particular from wine, characterized in that it comprises the following operating steps:

5 - preparing wine to be treated (V) inside a container (2);

10 - conveying said wine (V) to be treated to a unit (3) with hydrophobic membranes (4) having holes (5) for trapping gas (G) and able to be passed along, on a first side (4'), by said wine to be treated (V) and, on a second side (4''), by an extraction fluid (L) having an alcoholic content substantially similar to that of said wine (V) to be treated and made to circulate inside a purification circuit (8);

15 - removal of undesirable volatile substances from said wine to be treated (V) by means of evaporation and subsequent diffusion thereof in said gas (G) trapped in said membranes (4) and consequent condensation of said volatile substances on said second side (4'') of the membranes (4), with the formation of a contaminated fluid (L') formed by said extraction fluid (L) and by the permeated volatile substances, and a retained fraction formed by said treated wine (V') purified of said permeated volatile substances.

2. Process according to Claim 1, characterized in that it also comprises the step of re-introducing said treated wine (V') into said container (2).

3. Process according to Claim 1, characterized in that it also comprises the steps of:

- conveying said contaminated fluid (L') into a separation unit (9) by means of said purification circuit (8);

- removing said volatile substances from said contaminated fluid (L') with consequent regeneration of said extraction fluid (L);

- re-introducing said regenerated extraction fluid (L) into said purification circuit (8).

4. Process according to Claim 1, characterized in that said undesirable volatile substances consist of one or more components contained in the family comprising: acetic acid, ethyl acetate, acetaldehyde, sulphur dioxide, sulphurated organic compounds or other undesirable volatile compounds.

5. Process according to any one of the preceding claims, characterized in that said extraction fluid (L) consists of wine devoid of said undesirable substances.

6. Process according to Claim 3, characterized in that said step of removing said volatile substances from said contaminated fluid (L') is obtained by means of ion

exchange, in particular anion exchange.

7. Process according to one or more of Claims 1, 2 and 3, characterized in that said steps are repeated cyclically.

5 8. Process according to Claim 1, characterized in that said membranes (4) consist of hydrophobic polymers with a high molecular weight, such as polypropylene or polytetrafluoroethylene.

10 9. Plant for the separation of undesirable substances from alimentary liquids, in particular from wine, characterized in that it comprises:

- a container (2) for wine to be treated (V);
- a unit (3) having hydrophobic membranes (4), with holes (5) for trapping gas (G);
- 15 - first circulation means (6) for conveying said wine to be treated (V) through said unit (3), causing it to pass along a first side (4') of said membranes (4);
- second circulation means (7) for causing the flow of an extraction fluid (L) having an alcoholic content substantially similar to that of said wine to be treated (V), inside a purification circuit (3) through said unit (3), causing it to pass along the second side (4'') of said membranes (4);

25 said membranes (4) removing from said wine to be treated (V) said undesirable volatile substances by means

of evaporation and subsequent diffusion thereof in the gas (G) trapped in said membranes (4) and consequent condensation thereof on said second side (4") of said membranes (4), with the formation of a contaminated fluid 5 (L') formed by said extraction fluid (L) enriched with said permeated volatile substances, and a retained fraction (V') formed by said treated wine (V') purified of said volatile substances;

said purification circuit (8) supplying by means of 10 said second circulation means (7) at least one unit (9) for separation of said volatile substances from said contaminated fluid (L').

10. Plant according to Claim 9, characterized in that said separation unit (9) consists of an ion-exchange resin 15 filtration column.

11. Plant according to Claim 9, characterized in that said separation unit (9) consists of a distillation column.

12. Plant according to Claim 9, characterized in that said separation unit (9) consists of an ion-exchange resin 20 filtration unit or a unit for adsorption onto polymers.

13. Plant according to Claim 9, characterized in that said membranes (4) are formed by hydrophobic polymers with a high molecular weight, such as polypropylene or polytetrafluoroethylene.

25 14. Plant according to Claim 9, characterized in that

said purification circuit (8) is a closed circuit.

1/2

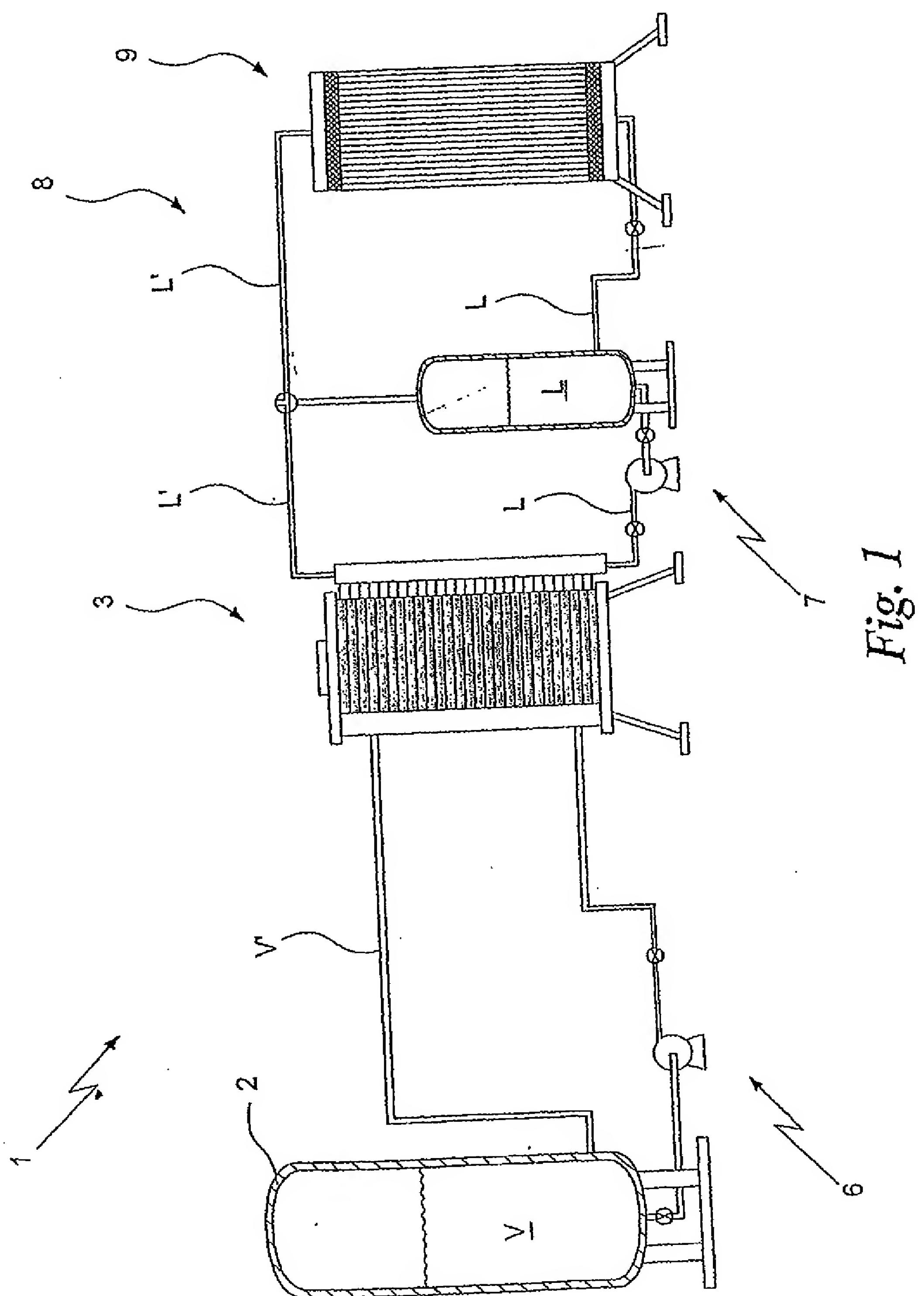


Fig. 1

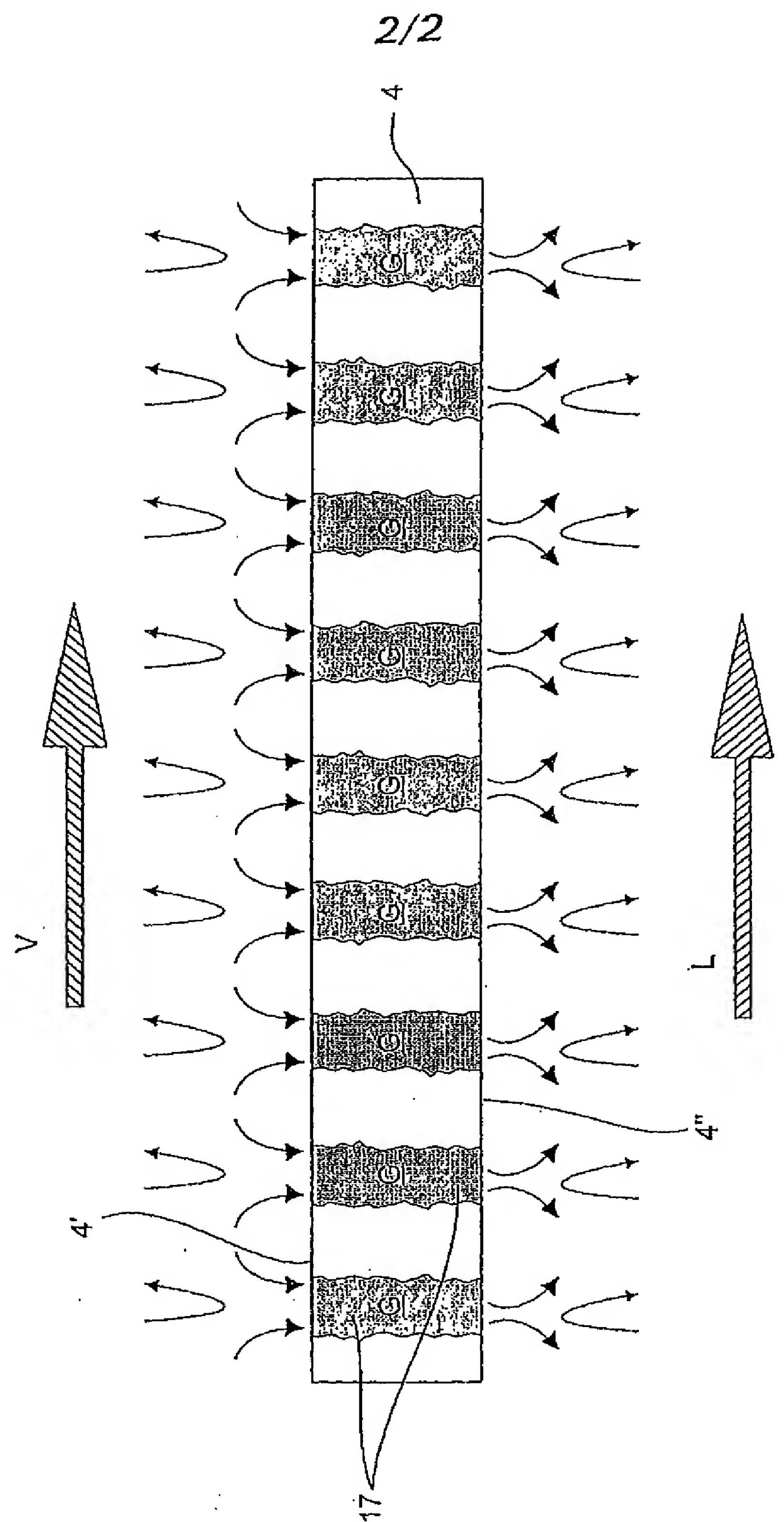


Fig. 2

INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.
PCT/IT 02/00472

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7	B01D63/00	B01D61/36	C12G3/08	C12H1/16
-------	-----------	-----------	----------	----------

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7	C12G	C12H
-------	------	------

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 22036 A (TYGOLA PTY LTD ;MICHAELS ALAN SHERMAN (US)) 11 November 1993 (1993-11-11) page 3, line 23 -page 4, line 12; examples ---	1,3,4, 7-9,13
Y	US 5 817 359 A (HOGAN PAUL ET AL) 6 October 1998 (1998-10-06) claims 1,18; example ---	2,5,6, 10-12
X	DE 41 09 080 C (RIPPERGER, SIEGFRIED) 26 November 1992 (1992-11-26) column 4, line 15 -column 5, line 15 ---	9,13,14
Y	---	2
A	---	1-8, 10-12
Y	---	5
A	---	1-4,6-14
	---	-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

*'T' later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*& document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the International search report
25 September 2002	07/10/2002
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 661 epo nl, Fax: (+31-70) 340-3016	Koch, J

INTERNATIONAL SEARCH REPORT

Inte	onal Application No
PCT/IT 02/00472	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 480 665 A (SMITH CLARK R) 2 January 1996 (1996-01-02) claims 1-3; figures 1,3 -----	6,10-12
A	WO 93 08257 A (GORE & ASS) 29 April 1993 (1993-04-29) example -----	1-14

INTERNATIONAL SEARCH REPORT

Int'l	onal Application No
PCT/IT 02/00472	

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
WO 9322036	A	11-11-1993	AU WO US ZA	4255993 A 9322036 A1 5817359 A 9303062 A	29-11-1993 11-11-1993 06-10-1998 10-11-1993
US 5817359	A	06-10-1998	AU WO ZA	4255993 A 9322036 A1 9303062 A	29-11-1993 11-11-1993 10-11-1993
DE 4109080	C	26-11-1992	DE	4109080 C1	26-11-1992
US 5480665	A	02-01-1996	AT AU AU BG BG CA DE DE DK EP ES HU WO ZA	171390 T 661912 B2 4231993 A 62318 B1 99165 A 2135305 A1 69321229 D1 69321229 T2 639105 T3 0639105 A1 2123053 T3 70805 A2 9323151 A1 9303213 A	15-10-1998 10-08-1995 13-12-1993 31-08-1999 28-08-1995 25-11-1993 29-10-1998 18-02-1999 14-06-1999 22-02-1995 01-01-1999 28-11-1995 25-11-1993 14-06-1994
WO 9308257	A	29-04-1993	AU AU CA DE DE EP JP US WO	654410 B2 2892592 A 2119898 A1 69209309 D1 69209309 T2 0609339 A1 7500283 T 5382364 A 9308257 A1	03-11-1994 21-05-1993 29-04-1993 25-04-1996 19-09-1996 10-08-1994 12-01-1995 17-01-1995 29-04-1993